

AN APPROXIMATE VARIATIONAL CALCULATION  
OF PROPERTIES OF THE  $1s\sigma$  AND  $2p\sigma$  STATES OF  $H_2^+$

by

Sungwoon Kim, Tai Yup Chang, and J. O. Hirschfelder

ABSTRACT

Calculations have been made for the energy of the hydrogen molecule ion at 54 internuclear separations ranging from 0 to  $20 a_0$  using the Guillemin and Zener approximate wave function<sup>1</sup>

$$\Psi_s = N_s [e^{-\alpha r_A - \beta r_B} + e^{-\alpha r_B - \beta r_A}]$$

for the  $1s\sigma$  ground state, and its anti-symmetric form

$$\Psi_p = N_p [e^{-\alpha r_A - \beta r_B} - e^{-\alpha r_B - \beta r_A}]$$

for the  $2p\sigma$  first excited state. The variational parameters,  $\alpha$  and  $\beta$  were varied to give the minimum energy. For the  $1s\sigma$  state, the Guillemin and Zener energy agrees with the exact energy to within 0.0005 ( $e^2/a_0$ ) for the full range of internuclear separations. For the  $2p\sigma$  state, at zero internuclear separation, the Guillemin and Zener energy (without nuclear repulsion energy) approaches  $-0.4 (e^2/a_0)$  instead of the correct value of  $-0.5 (e^2/a_0)$ . Thus, at small internuclear separations, the Guillemin and Zener energy for the  $2p\sigma$  state is not very accurate, but for inter-

nuclear separations larger than  $4 a_0$ , it is accurate to within 0.0001 ( $e^2/a_0$ ) .

Following a suggestion of Guillemin and Zener<sup>1</sup>, the energy was calculated varying only one parameter and fixing the value of the other by requiring that  $H\Psi$  remains finite at the nuclei. Using this method, the results for the  $1s\sigma$  state agree with the exact energy to within 0.001 ( $e^2/a_0$ ) for the full range of internuclear separations and to within 0.001 ( $e^2/a_0$ ) for the first excited state at internuclear separations larger than  $4 a_0$ . For the  $2p\sigma$  state this method gives less accurate results at smaller internuclear separations and fails to be applicable when the separation is less than  $1 a_0$ .

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The properties of the hydrogen molecule ion have been studied by many people. Some performed approximate calculation<sup>1-7</sup> and the others solved the exact equation<sup>8-13</sup>. V. Guillemin and C. Zener<sup>1</sup> have evaluated the  $1s\sigma$  ground state energy of the hydrogen molecule ion by the variational method with the approximate wave function

$$\Psi_s = N_s [e^{-\alpha r_A - \beta r_B} + e^{-\alpha r_B - \beta r_A}] \quad . \quad (1)$$

This Guillemin and Zener wave function has the correct limiting forms; at zero internuclear separation  $\Psi_s$  reduces to the  $1s$  wave function of  $He^+$ ,  $e^{-2r}$  with  $\alpha = \beta = 1$ ; and for infinite separation,  $\Psi_s$  reduces to the linear combination of the  $1s$  wave functions of hydrogen atoms,  $(e^{-r_A} + e^{-r_B})$  with  $\alpha = 1$  and  $\beta = 0$ . Thus, it seems as though this function might be useful as a good practical approximation to the cumbersome exact solution. Guillemin and Zener calculated the  $1s\sigma$  ground state energy at 11 internuclear separations (ranging from  $0.1 a_0$  to  $4 a_0$ ) to a precision of around  $0.001 (e^2/a_0)$ . Because  $\Psi_s$  is so simple and the corresponding energy is so accurate, it should have many applications. Therefore, we have repeated their calculation at 54 internuclear separations ranging from 0 to  $20 a_0$ .

to the greater precision of approximately  $0.000001 (e^2/a_0)$ .

In the "two parameter variation" method, the best values of the two parameters - those which make the energy minimum - were determined by fixing the value of the first parameter and varying the value of the second until the optimum value for the second (unfixed) parameter was found, then reversing the process - varying the first with the second fixed (using the value determined previously). This process is continued until a repetition produces a change in the energy which is less than the required tolerance.

The "one parameter variation" method corresponds to a suggestion of Guillemin and Zener<sup>1</sup> that a simple relation between the two parameters is obtained if  $H\Psi_s$  is required to be finite at the nuclei. This is a reasonable requirement since  $H\Psi$  is finite at the nuclei for the exact wave function. Consequently in this procedure, only one parameter is subjected to variation to give the minimum energy.

The same consideration has been given for the  $2p\sigma^-$  first excited state energy of the hydrogen molecule ion with the anti-symmetric form of the Guillemin and Zener approximate wave function

$$\Psi_p = N_p [e^{-\alpha r_A - \beta r_B} - e^{-\alpha r_B - \beta r_A}] \quad (2)$$

With the two parameter variation, the Guillemin and Zener energy for the  $1s\sigma^-$  state agrees with the exact energy to within  $0.0005 (e^2/a_0)$  for the full range of separations. For the  $2p\sigma^-$  state, at zero separation, the Guillemin and Zener energy

(without nuclear repulsion energy) approaches  $-0.4 (e^2/a_0)$  instead of the correct value of  $-0.5 (e^2/a_0)$ . Thus, the Guillemin and Zener energy for the  $2p\sigma$  state is not very accurate at small separations, but for separations larger than  $4 a_0$ , it is accurate to within  $0.0001 (e^2/a_0)$ .

Using the one parameter variation, the results for the  $1s\sigma$  state agree with the exact energy to within  $0.001 (e^2/a_0)$  for the full range of internuclear separations. For the  $2p\sigma$  state, the one parameter variation energy agrees with the exact to within  $0.001 (e^2/a_0)$  when the separation is greater than  $4 a_0$ , is less accurate at slightly smaller separation, and the method fails to be applicable when the separation is less than  $1 a_0$ .

### I. Ground State: $1s\sigma$

#### (a) Two Parameter Variation

The Guillemin and Zener approximate wave function<sup>1</sup> is used for the  $1s\sigma$  ground state of  $H_2^+$ :

$$\Psi_s = N_s [e^{-\alpha r_A - \beta r_B} + e^{-\alpha r_B - \beta r_A}] \quad (1)$$

where  $r_A$  and  $r_B$  are the distances to the electron from the nuclei A and B respectively,  $\alpha$  and  $\beta$  are variational parameters, and  $N_s$  is the normalization factor.

Introducing prolate spheroidal coordinates,

$$\lambda = (r_A + r_B) / R \quad (3)$$

$$\mu = (r_A - r_B) / R$$

and  $\Phi$ , the angle of rotation about the nuclear axis, the Hamiltonian is given by

$$H = \frac{-2}{R^2(\lambda^2 - \mu^2)} \left[ \frac{\partial}{\partial \lambda} (\lambda^2 - 1) \frac{\partial}{\partial \lambda} + \frac{\partial}{\partial \mu} (1 - \mu^2) \frac{\partial}{\partial \mu} + \frac{\lambda^2 - \mu^2}{(\lambda^2 - 1)(1 - \mu^2)} \frac{\partial^2}{\partial \Phi^2} + 2R\lambda \right] + \frac{1}{R} \quad (4)$$

and Eq. (1) can be written as

$$\Psi_s = 2 N_s e^{-a\lambda} \cosh(b\mu) \quad (5)$$

where

$$a = \frac{R}{2} (\alpha + \beta)$$

$$b = \frac{R}{2} (\beta - \alpha) \quad (6)$$

and  $R$  is internuclear distance.  $H\Psi_s$  has the following form:

$$H\Psi_s = \frac{-4N_s}{R^2(\lambda^2 - \mu^2)} e^{-a\lambda} \left[ \cosh(b\mu) \{ a^2\lambda^2 - b^2\mu^2 + 2(R-a)\lambda + (b^2 - a^2) \} \right. \\ \left. - 2b\mu \sinh(b\mu) \right] + \frac{1}{R} \Psi_s \quad (7)$$

The (1s $\sigma$  state) energy can be obtained by minimizing

$$E_s = \frac{\langle \Psi_s, H \Psi_s \rangle}{\langle \Psi_s, \Psi_s \rangle} \quad (8)$$

with respect to  $a$  and  $b$ .  $E_s$  is given by

$$E_s = \frac{4}{R^2} \frac{f_1}{f_2} + \frac{1}{R} \quad (9)$$

where

$$f_1 = \left( \frac{a}{2} - R - \frac{R}{2a} \right) \left( \frac{\sinh 2b}{2b} + 1 \right) + \frac{1}{4} (\cosh 2b + 1) - \frac{b^2}{3}$$

$$f_2 = \frac{1}{a} \left( 1 + \frac{1}{2a} \right) \left( \frac{\sinh 2b}{2b} + 1 \right) + \frac{1}{2b^2} \left( \cosh 2b - \frac{\sinh 2b}{2b} \right) + \frac{2}{3} \quad (10)$$

By varying the value of  $a$  for the given optimum value of  $b$  (the  $b$  obtained by one parameter variation may be used as a first approximation to the optimum value of  $b$ ) the approximate value of  $a$  making the energy minimum can be found. Next, by varying the value of  $b$  for the value of  $a$  obtained above, a more accurate value of  $b$  can be found, and so forth. The results obtained are given in Table 1 and compared with the exact ones of Bates, Ledsham and Stewart<sup>8</sup> which are obtained by exact expansion of the exact wave function.

#### (b) One Parameter Variation

By requiring that  $H\Psi_s$  remains finite at the nuclei and putting  $\lambda = \mu = 1$  in Eq. (7), the following simple relation

between  $a$  and  $b$  is obtained:

$$a = R - b \tanh b \quad (11)$$

The optimum value of  $b$  is obtained by setting

$$\frac{dE_s}{db} = \frac{\partial E_s}{\partial b} + \frac{\partial E_s}{\partial a} \frac{da}{db} = 0 \quad (12)$$

From Eq. (9) this becomes

$$(f_2 \frac{\partial f_1}{\partial b} - f_1 \frac{\partial f_2}{\partial b}) + (f_2 \frac{\partial f_1}{\partial a} - f_1 \frac{\partial f_2}{\partial a}) \frac{da}{db} = 0 \quad (13)$$

where

$$\frac{\partial f_1}{\partial b} = \frac{1}{b} \left( \frac{a}{2} - R - \frac{R}{2a} \right) \left( \cosh 2b - \frac{\sinh 2b}{2b} \right) + \frac{\sinh 2b}{2} - \frac{2}{3} b$$

$$\frac{\partial f_2}{\partial b} = \frac{1}{b} \left( \frac{1}{a} + \frac{1}{2a^2} - \frac{3}{2b^2} \right) \left( \cosh 2b - \frac{\sinh 2b}{2b} \right) + \frac{1}{b^2} \sinh 2b$$

$$\frac{\partial f_1}{\partial a} = \frac{1}{2} \left( 1 + \frac{R}{a^2} \right) \left( \frac{\sinh 2b}{2b} + 1 \right)$$

$$\frac{\partial f_2}{\partial a} = -\frac{1}{a^2} \left( 1 + \frac{1}{a} \right) \left( \frac{\sinh 2b}{2b} + 1 \right) \quad (14)$$

and from Eq. (11) it follows that

$$\frac{da}{db} = - \frac{\sinh 2b + 2b}{\cosh 2b + 1} \quad (15)$$

Using Eqs. (9), (11) and (13), the values of  $a$  and  $b$  which

make  $E$  minimum for given  $R$  are obtained. With these  $a$  and  $b$  the ( $1s\sigma$  state) energy is calculated. The results are tabulated in Table 1 and compared with the exact values of Bates, Ledsham and Stewart.<sup>8</sup>

### (c) Fixed Parameter

Special interest is attached to two special cases of the Guillemin and Zener wave function:

$$1) \Phi_s = e^{-r_A - r_B} \text{ corresponding to } a=R \text{ and } b=0 (\alpha=\beta=1).$$

As  $R$  becomes zero,  $\Phi_s$  becomes the correct wave function for  $H_2^+$  or  $He^+$ . The energy is given by

$$E_s = - \frac{1+2R}{\frac{1}{2}+R+\frac{2}{3}R^2} + \frac{1}{R} \quad (16)$$

Numerical values of  $E_s$  as a function of  $R$  are given in Table 2 and shown in Fig. 1.

2) The Pauling function<sup>14</sup>  $\chi_s = e^{-r_A} + e^{-r_B}$  corresponding to  $a = \frac{R}{2} = -b$  ( $\alpha=1$  and  $\beta=0$ ). As  $R$  becomes infinite,  $\chi_s$  becomes the correct limiting form for the  $H_2^+$  wave function. The energy is given by

$$E_s = \frac{-3(4+3R)(R+\sinh R)+3R(1+\cosh R)-R^3}{6(1+R)(R+\sinh R)+6(R\cosh R-\sinh R)+2R^3} + \frac{1}{R} \quad (17)$$

Numerical values of  $E_s$  as a function of  $R$  are given in Table 3 and shown in Fig. 1.

II. First Excited State:  $2p\sigma$

(a) Two Parameter Variation

The approximate wave function which is employed for the  $2p\sigma$  first excited state of  $H_2^+$  is

$$\Psi_p = N_p [e^{-\alpha r_A - \beta r_B} - e^{-\alpha r_B - \beta r_A}] \quad (2)$$

or

$$\Psi_p = 2 N_p e^{-\alpha \lambda} \sinh(b\mu) \quad (18)$$

where  $a$  and  $b$  are given by Eq. (6).  $H\Psi_p$  is given by

$$H\Psi_p = -\frac{4 N_p}{R^2(\lambda^2 - \mu^2)} e^{-\alpha \lambda} [\sinh(b\mu) \{a^2 \lambda^2 - b^2 \mu^2 + 2(R-a)\lambda + (b^2 - a^2)\} - 2b\mu \cosh(b\mu)] + \frac{1}{R} \Psi_p. \quad (19)$$

$E_p$  is given by

$$E_p = \frac{4}{R^2} \frac{f_3}{f_4} + \frac{1}{R} \quad (20)$$

where

$$f_3 = \left( \frac{a}{2} + \frac{1}{4} - R - \frac{R}{2a} \right) \left( \frac{\sinh 2b}{2b} - 1 \right) + \frac{1}{4} \left( \cosh 2b - \frac{\sinh 2b}{2b} \right) + \frac{b^2}{3}$$

$$f_4 = \frac{1}{a} \left( 1 + \frac{1}{2a} \right) \left( \frac{\sinh 2b}{2b} - 1 \right) + \frac{1}{2b^2} \left( \cosh 2b - \frac{\sinh 2b}{2b} \right) - \frac{2}{3} \quad (21)$$

The two parameter variation energy is calculated using Eqs. (20) and (21). In Table 4 the results are tabulated and compared with the exact values of Bates, Ledsham and Stewart<sup>8</sup>.  $E_p$  as a function of  $R$  is plotted in Fig. 2.

In the limit as  $R \rightarrow 0$ , we can expand  $r_A$  and  $r_B$  in the Taylor's series

$$\begin{aligned} r_A &= r + \frac{R}{2} \cos \theta + \dots \\ r_B &= r - \frac{R}{2} \cos \theta + \dots \end{aligned} \quad (22)$$

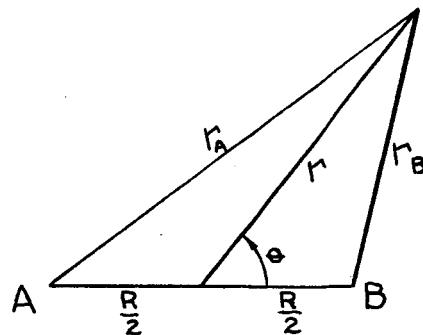


Fig. 3

as shown in Fig. 3. Then  $\Psi_p$  becomes

$$\Psi_p = -N_p e^{-(\alpha+\beta)r} [(\alpha-\beta)R \cos \theta + O(R^2)] \quad (23)$$

Thus  $\Psi_p$  approaches the limiting form

$$\Psi_p = N'_p e^{-cr} \cos \theta, \quad R=0 \quad (24)$$

Here  $c$  is the variational parameter. The energy, which does not include internuclear repulsive energy, is given by

$$\left(E_p - \frac{1}{R}\right)_{R=0} = \left(\frac{5}{2}c - 2\right)c \quad (25)$$

Thus, the limiting value of  $(E_p - 1/R)_{R=0}$  is found to be  $-0.4 (e^2/a_0)$ , instead of the correct value  $-0.5 (e^2/a_0)$ . As a result, it is apparent that the two parameter energy for the  $2p\sigma$  state cannot be accurate at small separation. Indeed in Table 4, the error in  $E_p$  is greater than  $0.001 (e^2/a_0)$  when  $R < 2.5 a_0$ .

#### (b) One Parameter Variation

Again, by requiring  $H\Psi_p$  to take a finite value at the nuclei, the following equation is obtained:

$$a = R - \frac{b}{\tanh b} \quad (26)$$

This condition can only be satisfied if  $R \geq 1$ . Hence the one parameter variation procedure is only applicable for  $R \geq 1$  and only accurate for large values of  $R$ . For  $R \leq 1$ , the value of  $a$  is necessarily negative since  $b/\tanh b$  is never less than 1. If  $a$  were negative  $\Psi_p$  would approach infinity for large values of  $\lambda$  and would not satisfy the boundary conditions required of a bound state wave function.

For  $R > 1$ , the energy is given by Eq. (20) where the parameter  $a$  is given by Eq. (26). The optimum value of  $b$  is

obtained by setting

$$\frac{dE_p}{db} = \frac{\partial E_p}{\partial b} + \frac{\partial E_p}{\partial a} \frac{da}{db} = 0 \quad (27)$$

From Eq. (20) this becomes

$$\left( f_4 \frac{\partial f_3}{\partial b} - f_3 \frac{\partial f_4}{\partial b} \right) + \left( f_4 \frac{\partial f_3}{\partial a} - f_3 \frac{\partial f_4}{\partial a} \right) \frac{da}{db} = 0 \quad (28)$$

where

$$\begin{aligned} \frac{\partial f_3}{\partial b} &= \frac{1}{b} \left( \frac{a}{2} - R - \frac{R}{2a} \right) \left( \cosh 2b - \frac{\sinh 2b}{2b} \right) + \frac{\sinh 2b}{2} + \frac{2}{3} b \\ \frac{\partial f_4}{\partial b} &= \frac{1}{b} \left( \frac{1}{a} + \frac{1}{2a^2} - \frac{3}{2b^2} \right) \left( \cosh 2b - \frac{\sinh 2b}{2b} \right) + \frac{1}{b^2} \sinh 2b \\ \frac{\partial f_3}{\partial a} &= \frac{1}{2} \left( 1 + \frac{R}{a^2} \right) \left( \frac{\sinh 2b}{2b} - 1 \right) \\ \frac{\partial f_4}{\partial a} &= -\frac{1}{a^2} \left( 1 + \frac{1}{a} \right) \left( \frac{\sinh 2b}{2b} - 1 \right) \end{aligned} \quad (29)$$

And from Eq. (26) it follows that

$$\frac{da}{db} = \frac{2b - \sinh 2b}{\cosh 2b - 1} \quad (30)$$

The results for the one parameter (as well as the two parameter) variation are tabulated and compared with the exact values of Bates, Ledsham and Stewart<sup>8</sup> in Table 4 and plotted in Fig. 2.

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TABLE 1

1s $\sigma$  GROUND STATE OF H<sub>2</sub><sup>+</sup>

The values not in the brackets are obtained by two parameter variation method, and those in the brackets, ( ) are obtained by one parameter variation method.  $(E - 1/R)_{\text{Exact}}$  are the results of Bates, Ledsham and Stewart.<sup>8</sup>

R(a <sub>0</sub> )	$\alpha$	$b$	$\alpha$	$\beta$	$E_s(e^2/a_0)$	$(E_s - \frac{1}{R})(e^2/a_0)$	$(E - \frac{1}{R})_{\text{Exact}}(e^2/a_0)$
0.1	0.0990	0.0570		0.4200	1.5600	8.02177	-1.97822
	(0.0989)	(0.0317)		(0.6729)	(1.3069)	(8.02177)	(-1.97822)
0.2	0.19383	0.1135		0.4016	1.5366	3.07146	-1.92853
	(0.1937)	(0.0789)		(0.5740)	(1.3637)	(3.07147)	(-1.92852)
0.3	0.2834	0.1678		0.3854	1.5041	1.46679	-1.86654
	(0.2832)	(0.1296)		(0.5120)	(1.3764)	(1.46682)	(-1.86650)
0.4	0.3680	0.2201		0.3698	1.4703	0.69947	-1.80052
	(0.3676)	(0.1807)		(0.4674)	(1.3710)	(0.69953)	(-1.8004)
0.5	0.4480	0.2707		0.3547	1.4375	0.26528	-1.73471
	(0.4475)	(0.2311)		(0.4328)	(1.3572)	(0.26536)	(-1.73463)
0.6	0.5241	0.3197		0.3407	1.4064	-0.00451	-1.67118
	(0.5233)	(0.2805)		(0.4046)	(1.3397)	(-0.00442)	(-1.67109)

TABLE I (cont'd)

$R(a_0)$	$a$	$b$	$\alpha$	$\beta$	$E_s(e^2/a_0)$	$(E_s - \frac{1}{R})(e^2/a_0)$	$(E - \frac{1}{R})_{\text{exact}}(e^2/a_0)$
0.7	0.5967 (0.5955)	0.3673 (0.3288)	0.3277 (0.3809)	1.3771 (1.3206)	-0.18231 (-0.18221)	-1.61088 (-1.61078)	
0.8	0.6662 (0.6647)	0.4136 (0.3762)	0.3156 (0.3605)	1.3498 (1.3012)	-0.30416 (-0.30405)	-1.55416 (-1.55405)	-1.55448
0.9	0.7330 (0.7311)	0.4589 (0.4228)	0.3045 (0.3426)	1.3243 (1.2822)	-0.38996 (-0.38985)	-1.50107 (-1.50096)	
1.0	0.7974 (0.7952)	0.5033 (0.4685)	0.2941 (0.3266)	1.3007 (1.2637)	-0.45148 (-0.45137)	-1.45148 (-1.45137)	-1.45178
1.1	0.8597 (0.8571)	0.5469 (0.5136)	0.2843 (0.3122)	1.2787 (1.2461)	-0.49612 (-0.49601)	-1.40521 (-1.40510)	
1.2	0.9200 (0.9171)	0.5897 (0.5582)	0.2752 (0.2991)	1.2581 (1.2294)	-0.52869 (-0.52859)	-1.36202 (-1.36193)	-1.36231
1.3	0.9787 (0.9755)	0.6321 (0.6022)	0.2666 (0.2871)	1.2390 (1.2137)	-0.55247 (-0.55238)	-1.32170 (-1.32161)	

TABLE I (cont'd)

$R(a_0)$	$a$	$b$	$\alpha$	$\beta$	$E_s(e^2/a_0)$	$(E_s - \frac{1}{R})(e^2/a_0)$	$(E - \frac{1}{R})$ Exact ( $e^2/a_0$ )
1.4	1.0358 (1.0324)	0.6739 (0.6460)	0.2585 (0.2760)	1.2213 (1.1988)	-0.56972 (-0.56964)	-1.28401 (-1.28393)	-1.28427
1.5	1.0916 (1.0879)	0.7153 (0.6894)	0.2508 (0.2657)	1.2046 (1.1849)	-0.58208 (-0.58200)	-1.24874 (-1.24867)	
1.6	1.1461 (1.1423)	0.7565 (0.7326)	0.2435 (0.2560)	1.1892 (1.1718)	-0.59070 (-0.59064)	-1.21570 (-1.21564)	-1.21593
1.7	1.1995 (1.1956)	0.7974 (0.7756)	0.2365 (0.2467)	1.1747 (1.1595)	-0.59647 (-0.59642)	-1.18471 (-1.18466)	
1.8	1.2519 (1.2480)	0.8381 (0.8185)	0.2298 (0.2385)	1.1611 (1.1481)	-0.60004 (-0.60000)	-1.15560 (-1.15555)	-1.15581
1.9	1.3033 (1.2995)	0.8787 (0.8614)	0.2234 (0.2305)	1.1485 (1.1373)	-0.60244 (-0.60187)	-1.10307 (-1.12818)	
2.0	1.3540 (1.3503)	0.9191 (0.9042)	0.2174 (0.2230)	1.1365 (1.1273)	-0.60244 (-0.60241)	-1.10244 (-1.10242)	-1.10263
2.1	1.4038 (1.4005)	0.9593 (0.9471)	0.2116 (0.2158)	1.1253 (1.1179)	-0.60195 (-0.60193)	-1.07814 (-1.07812)	

TABLE I (cont'd)

$R(a_0)$	$1s\sigma$	GROUND STATE OF $H_2^+$	$E_s(e^2/a_0)$	$(E_s - \frac{1}{R})(e^2/a_0)$	$(E - \frac{1}{R})$ Exact $(e^2/a_0)$
2.2	1.4529 (1.4501)	0.9997 (0.9900)	0.2060 (0.2091)	1.1148 (1.1091)	-0.60066 (-0.60065)
2.3	1.5014 (1.4992)	1.0431 (1.0330)	0.2005 (0.2026)	1.1051 (1.1009)	-0.59875 (-0.59875)
2.4	1.5494 (1.5478)	1.0806 (1.0762)	0.1953 (0.1965)	1.0958 (1.0933)	-0.59638 (-0.59638)
2.5	1.5968 (1.5961)	1.1212 (1.1194)	0.1902 (0.1906)	1.0872 (1.0862)	-0.59365 (-0.59365)
2.6	1.6437 (1.6441)	1.1620 (1.1629)	0.1852 (0.1850)	1.0791 (1.0796)	-0.59067 (-0.59067)
2.7	1.6903 (1.6917)	1.2029 (1.2065)	0.1805 (0.1797)	1.0715 (1.0734)	-0.58749 (-0.58749)
2.8	1.7364 (1.7392)	1.2440 (1.2503)	0.1758 (0.1746)	1.0644 (1.0677)	-0.58419 (-0.58419)
2.9	1.7822 (1.7865)	1.2853 (1.2943)	0.1713 (0.1697)	1.0577 (1.0623)	-0.58081 (-0.58080)
					-0.94150 (-0.94133)
					-0.92564 (-0.92563)

TABLE I (cont'd)

$R(a_0)$	a	b	$\alpha$	$\beta$	$E_s(e^2/a_0)$	$(E_s - \frac{1}{R})(e^2/a_0)$	$(E - \frac{1}{R})_{\text{Exact}}(e^2/a_0)$
3.0	1.8277 (1.8336)	1.3269 (1.3386)	0.1669 (0.1650)	1.0515 (1.0574)	-0.57740 (-0.57783)	-0.91073 (-0.91072)	-0.91089
3.5	2.0520 (2.0675)	1.5392 (1.5637)	0.1465 (0.1439)	1.0260 (1.0375)	-0.56067 (-0.56061)	-0.84639 (-0.84632)	
4.0	2.2733 (2.3000)	1.7605 (1.7962)	0.1282 (0.1259)	1.0084 (1.0240)	-0.54587 (-0.54575)	-0.79587 (-0.79575)	-0.79608
4.5	2.4944 (2.5313)	1.9921 (2.0367)	0.1116 (0.1099)	0.9970 (1.0151)	-0.53369 (-0.53352)	-0.75592 (-0.75574)	
5.0	2.7171 (2.7616)	2.2342 (2.2852)	0.0965 (0.0952)	0.9902 (1.0093)	-0.52415 (-0.52395)	-0.72415 (-0.72395)	-0.72442
5.5	2.9428 (2.9908)	2.4862 (2.5405)	0.0830 (0.0818)	0.9871 (1.0057)	-0.51694 (-0.51676)	-0.69876 (-0.69858)	-0.69905
6.0	3.1717 (3.2197)	2.7461 (2.8008)	0.0709 (0.0698)	0.9863 (1.0034)	-0.51169 (-0.51153)	-0.67835 (-0.67820)	-0.67863
6.5	3.4041 (3.4492)	3.0118 (3.0641)	0.0603 (0.0592)	0.9870 (1.0020)	-0.50796 (-0.50784)	-0.66180 (-0.66169)	-0.66206

TABLE I (cont'd)

$R(a_0)$	$a$	$b$	$\alpha$	$\beta$	$E_s(e^2/a_0)$	$(E_s - \frac{1}{R})(e^2/a_0)$	$(E - \frac{1}{R})_{\text{Exact}}(e^2/a_0)$
7.0	3.6394 (3.6800)	3.2805 (3.3284)	0.0512 (0.0502)	0.9885 (1.0012)	-0.50537 (-0.50529)	-0.64823 (-0.64815)	-0.64845
7.5	3.8774 (3.9128)	3.5501 (3.5925)	0.0436 (0.0427)	0.9903 (1.0007)	-0.50361 (-0.50355)	-0.63694 (-0.63689)	-0.63713
8.0	4.1175 (4.1478)	3.8190 (3.8556)	0.0373 (0.0365)	0.9920 (1.0004)	-0.50242 (-0.50239)	-0.62742 (-0.62739)	-0.62757
8.5	4.3594 (4.3849)	4.0861 (4.1172)	0.0321 (0.0314)	0.9935 (1.0002)	-0.50163 (-0.50161)	-0.61928 (-0.61926)	-0.61939
9.0	4.6024 (4.6240)	4.3510 (4.3773)	0.0279 (0.0274)	0.9948 (1.0001)	-0.50110 (-0.50109)	-0.61222 (-0.61220)	-0.61231
9.5	4.8464 (4.8647)	4.6141 (4.6360)	0.0244 (0.0240)	0.9958 (1.0000)	-0.50076 (-0.50075)	-0.60602 (-0.60601)	
10.0	5.0915 (5.1069)	4.8750 (4.8935)	0.0216 (0.0213)	0.9966 (1.0000)	-0.50052 (-0.50052)	-0.60052 (-0.60052)	
11.0	5.5835 (5.5945)	5.3920 (5.4056)	0.0174 (0.0171)	0.9977 (1.0000)	-0.50026 (-0.50026)	-0.59117 (-0.59117)	

TABLE I (cont'd)

$R(a_0)$	$a$	$b$	$\alpha$	$\beta$	$E_s(e^2/a_0)$	$(E_s - \frac{1}{R})(e^2/a_0)$	$(E - \frac{1}{R})_{\text{Exact}}(e^2/a_0)$
12.0	6.0765 (6.0852)	5.9050 (5.9148)	0.0142 (0.0142)	0.9984 (1.0000)	-0.50015 (-0.50014)	-0.58348 (-0.58348)	
13.0	6.5705 (6.5779)	6.4140 (6.4220)	0.0120 (0.0119)	0.9988 (1.0000)	-0.50009 (-0.50009)	0.57701 (-0.57701)	
14.0	7.0665 (7.0719)	6.9210 (6.9280)	0.0103 (0.0102)	0.9991 (1.0000)	-0.50006 (-0.50006)	-0.57148 (-0.57148)	
15.0	7.5625 (7.5669)	7.4270 (7.4330)	0.0090 (0.0089)	0.9993 (1.0000)	-0.50004 (-0.50004)	-0.56670 (-0.56670)	
16.0	8.0585 (8.0627)	7.9330 (7.9373)	0.0078 (0.0078)	0.9994 (1.0000)	-0.50003 (-0.50003)	-0.56253 (-0.56253)	
17.0	8.5555 (8.5589)	8.4370 (8.4410)	0.0069 (0.0069)	0.9995 (1.0000)	-0.50002 (-0.50002)	-0.55884 (-0.55884)	
18.0	9.0525 (9.0556)	8.9410 (8.9443)	0.0061 (0.0061)	0.9996 (1.0000)	-0.50001 (-0.50001)	-0.55557 (-0.55557)	
19.0	9.5495 (9.5527)	9.4440 (9.4473)	0.0055 (0.0055)	0.9996 (1.0000)	-0.50001 (-0.50001)	-0.55264 (-0.55264)	
20.0	10.0475 (10.0501)	9.9470 (9.9499)	0.0050 (0.0050)	0.9997 (1.0000)	-0.50001 (-0.50001)	-0.55001 (-0.55001)	

TABLE 2

The energy corresponding to the  $1s\sigma$  ground state of  $H_2^+$  using the wave function  $\phi_s = e^{-\frac{r}{a} - \frac{r}{b}}$ . This corresponds to the special case of the Guillemin and Zener function when  $a = R$  and  $b = 0$  ( $\alpha = \beta = 1$ ). Here  $E_s$  is given by Eq. (16).

$R (a_0)$	$E_s (e^2/a_0)$	$(E_s - \frac{1}{R})(e^2/a_0)$
0.1	8.0219	-1.9780
0.2	3.0733	-1.9266
0.3	1.4728	-1.8604
0.4	0.7119	-1.7880
0.5	0.2857	-1.7142
0.6	0.0248	-1.6417
0.7	-0.1434	-1.5720
0.8	-0.2557	-1.5057
0.9	-0.3321	-1.4432
1.0	-0.3846	-1.3846
1.1	-0.4205	-1.3299
1.2	-0.4448	-1.2781
1.3	-0.4608	-1.2300
1.4	-0.4707	-1.1850
1.5	-0.4761	-1.1428
1.6	-0.4783	-1.1033
1.7	-0.4780	-1.0662
1.8	-0.4758	-1.0313
1.9	-0.4722	-0.9986

TABLE 2 (cont'd)

$R (a_0)$	$E_s (e^2/a_0)$	$(E_s - \frac{1}{R})(e^2/a_0)$
2.0	-0.4677	-0.9677
2.1	-0.4624	-0.9386
2.2	-0.4565	-0.9111
2.3	-0.4503	-0.8851
2.4	-0.4438	-0.8605
2.5	-0.4372	-0.8372
2.6	-0.4304	-0.8150
2.7	-0.4236	-0.7940
2.8	-0.4168	-0.7740
2.9	-0.4101	-0.7549
3.0	-0.4035	-0.7368
3.5	-0.3718	-0.6575
4.0	-0.3434	-0.5934
4.5	-0.3183	-0.5405
5.0	-0.2962	-0.4962
5.5	-0.2767	-0.4585
6.0	-0.2595	-0.4262
6.5	-0.2442	-0.3981
7.0	-0.2305	-0.3734
7.5	-0.2183	-0.3516
8.0	-0.2072	-0.3322
8.5	-0.1972	-0.3148
9.0	-0.1881	-0.2992

TABLE 2 (cont'd)

$R (a_0)$	$E_s (e^2/a_0)$	$(E_s - \frac{1}{R}) (e^2/a_0)$
9.5	-0.1797	-0.2850
10.0	-0.1721	-0.2721
11.0	-0.1586	-0.2495
12.0	-0.1470	-0.2304
13.0	-0.1370	-0.2140
14.0	-0.1283	-0.1997
15.0	-0.1206	-0.1873
16.0	-0.1138	-0.1763
17.0	-0.1077	-0.1665
18.0	-0.1022	-0.1577
19.0	-0.0972	-0.1499
20.0	-0.0927	-0.1427

TABLE 3

The energy corresponding to the Pauling wave function  
 $\chi_s = e^{-\frac{R}{2}} + e^{-\frac{R}{2}}$  for the 1s ground state  
 of  $H_2^+$ . This wave function is a special case of the  
 Guillemin and Zener function with  $a = \frac{R}{2} = b$  ( $a=1$  and  $\beta=0$ ).  
 $E_s$  is given by Eq. (17).

$R (a_0)$	$E_s (e^2/a_0)$	$(E_s - \frac{1}{R})(e^2/a_0)$
0.1	8.5045	-1.4954
0.2	3.5164	-1.4835
0.3	1.8671	-1.4662
0.4	1.0549	-1.4450
0.5	0.5786	-1.4213
0.6	0.2707	-1.3958
0.7	0.0591	-1.3694
0.8	-0.0924	-1.3424
0.9	-0.2042	-1.3153
1.0	-0.2883	-1.2883
1.1	-0.3527	-1.2617
1.2	-0.4024	-1.2357
1.3	-0.4411	-1.2103
1.4	-0.4713	-1.1856
1.5	-0.4950	-1.1616
1.6	-0.5135	-1.1385
1.7	-0.5279	-1.1161
1.8	-0.5390	-1.0945
1.9	-0.5474	-1.0737

TABLE 3 (cont'd)

$R (a_0)$	$E_s (e^2/a_0)$	$(E_s - \frac{1}{R}) (e^2/a_0)$
2.0	-0.5537	-1.0537
2.1	-0.5583	-1.0345
2.2	-0.5614	-1.0160
2.3	-0.5634	-0.9982
2.4	-0.5645	-0.9812
2.5	-0.5648	-0.9648
2.6	-0.5644	-0.9491
2.7	-0.5636	-0.9340
2.8	-0.5624	-0.9195
2.9	-0.5608	-0.9057
3.0	-0.5590	-0.8924
3.5	-0.5481	-0.8338
4.0	-0.5368	-0.7868
4.5	-0.5270	-0.7492
5.0	-0.5192	-0.7192
5.5	-0.5133	-0.6951
6.0	-0.5090	-0.6757
6.5	-0.5060	-0.6599
7.0	-0.5040	-0.6468
7.5	-0.5026	-0.6359
8.0	-0.5017	-0.6267
8.5	-0.5011	-0.6187

TABLE 3 (cont'd)

$R (a_0)$	$E_s (e^2/a_0)$	$(E_s - \frac{1}{R}) (e^2/a_0)$
9.0	-0.5007	-0.6118
9.5	-0.5004	-0.6057
10.0	-0.5002	-0.6002
11.0	-0.5001	-0.5910
12.0	-0.5000	-0.5833
13.0	-0.5000	-0.5769
14.0	-0.5000	-0.5714
15.0	-0.5000	-0.5666
16.0	-0.5000	-0.5625
17.0	-0.5000	-0.5588
18.0	-0.5000	-0.5555
19.0	-0.5000	-0.5526
20.0	-0.5000	-0.5500

TABLE 4

2p $\sigma$  FIRST EXCITED STATE OF H<sub>2</sub><sup>+</sup>

The values not in the brackets are obtained by two parameter variation method, and those in the brackets, ( ) are obtained by one parameter variation method. ( $E - 1/R$ )<sub>Exact</sub> are the results of Bates, Ledsham and Stewart.<sup>8</sup>

$R(a_0)$	$a$	$b$	$\alpha$	$\beta$	$E_p(e^2/a_0)$	$(E_p - \frac{1}{R})(e^2/a_0)$	$(E - \frac{1}{R})(e^2/a_0)$ Exact
0.1	0.0209	0.0232	-0.0220	0.4419	9.58691	-0.41308	
0.2	0.0441	0.0668	-0.1133	0.5546	4.57328	-0.42671	-0.50268
0.4	0.0976	0.1478	-0.1253	0.6136	2.04447	-0.45552	-0.51079
0.6	0.1623	0.2288	-0.1107	0.6519	1.18064	-0.48602	-0.52431
0.8	0.2393	0.3158	-0.0953	0.6939	0.73254	-0.51745	-0.54274
1.0	0.3290	0.4068	-0.0777	0.7358	0.45127	-0.54872	-0.56481
1.2	0.4301	0.5018	-0.0597	0.7766	0.25476	0.57857	-0.58861
(0.1998)	(0.0186)	(0.1510)	(0.1820)	(0.39121)	(-0.44212)		
1.4	0.5405	0.5998	-0.0423	0.8145	0.10845	-0.60583	-0.61208
(0.3998)	(0.0193)	(0.2718)	(0.2994)	(0.13850)	(-0.57577)		
1.6	0.6573	0.7008	-0.0271	0.8488	-0.00466	0.62966	-0.63361
(0.5993)	(0.0454)	(0.3461)	(0.4029)	(-0.0043)	(-0.62543)		

TABLE 4 (cont'd)

 $2p\sigma'$  FIRST EXCITED STATE OF  $H_2^+$ 

$R(a_0)$	$a$	$b$	$\alpha$	$\beta$	$E_p(e^2/a_0)$	$(E_p - \frac{1}{R})(e^2/a_0)$	$(E - \frac{1}{R})(e^2/a_0)$ Exact
1.8	0.7780 (0.7657)	0.8018 (0.3217)	-0.0132 (0.2466)	0.8776 (0.6041)	-0.09410 (-0.09274)	-0.64966 (-0.64829)	-0.65223
2.0	0.9003 (0.8871)	0.9042 (0.5883)	-0.0019 (0.1494)	0.9022 (0.7377)	-0.16581 (-0.16482)	-0.66581 (-0.66482)	-0.66754
2.2	1.0229	1.0066	0.0074	0.9225	-0.22382	-0.67836	-0.67956
2.4	1.1448	1.1088	0.0150	0.9390	-0.27105	-0.68772	-0.68858
2.6	1.2654	1.2105	0.0211	0.9522	-0.30971	-0.69433	-0.69496
2.8	1.3845 (1.3690)	1.3118 (1.1873)	0.0259 (0.0649)	0.9629 (0.9129)	-0.34149 (-0.34117)	-0.69864 (-0.69832)	-0.69911
3.0	1.5018 (1.4861)	1.4126 (1.3073)	0.0297 (0.0595)	0.9714 (0.9311)	-0.36771 (-0.36747)	-0.70105 (-0.70080)	-0.70143

TABLE 4. (cont'd)

 $2p\sigma$  FIRST EXCITED STATE OF  $H_2^+$ 

$R(a_0)$	$a$	$b$	$\alpha$	$\beta$	$E_p(e^2/a_0)$	$(E_p - \frac{1}{R})(e^2/a_0)$	$(E - \frac{1}{R})(e^2/a_0)$	Exact
3.2	1.6174	1.5128	0.0326	0.9781	-0.38942	-0.70192		
3.4	1.7312	1.6112	0.0348	0.9834	-0.40744	-0.70156		
3.5	(1.7719)	(1.5900)	(0.0519)	(0.9605)	(-0.41515)	(-0.70086)		
3.6	1.8435	1.7120	0.0365	0.9876	-0.42244	-0.70022		
3.8	1.9543	1.8110	0.0377	0.9908	-0.43495	-0.69811		
4.0	2.0637	1.9097	0.0385	0.9933	-0.44541	-0.69541	-0.69555	
	(2.0490)	(1.8583)	(0.0476)	(0.9768)	(-0.44534)	(-0.69534)		
4.5	2.3320	2.1556	0.0392	0.9972	-0.46473	-0.68695		
	(2.3188)	(2.1190)	(0.0443)	(0.9862)	(-0.46469)	(-0.68692)		
5.0	2.5940	2.4009	0.0386	0.9989	-0.47722	-0.67722	-0.67729	
	(2.5830)	(2.3755)	(0.0415)	(0.9917)	(-0.47720)	(-0.67720)		
5.5	2.8512	2.6464	0.0372	0.9995	-0.48532	-0.66714	-0.66719	
	(2.8429)	(2.6295)	(0.0387)	(0.9950)	(-0.48532)	(-0.66714)		

TABLE 4 (cont'd)  
 $2p\sigma$  FIRST EXCITED STATE OF  $H_2^+$

$R(a_0)$	$a$	$b$	$\alpha$	$\beta$	$E_p(e^2/a_0)$	$(E_p - \frac{1}{R})(e^2/a_0)$	$(E - \frac{1}{R})(e^2/a_0)$
6.0	3.1050	2.8925	0.0354	0.9995	-0.49059	-0.65726	-0.65731
	(3.0994)	(2.8824)	(0.0361)	(0.9969)	(-0.49059)	(-0.65726)	
6.5	3.3562	3.1395	0.0333	0.9993	-0.49402	-0.64786	-0.64791
	(3.3533)	(3.1348)	(0.0336)	(0.9981)	(-0.49402)	(-0.64786)	
7.0	3.6056	3.3878	0.0311	0.9990	-0.49623	-0.63909	-0.63913
	(3.6051)	(3.3870)	(0.0311)	(0.9988)	(-0.49623)	(-0.63909)	
7.5	3.8538	3.6371	0.0288	0.9987	-0.49766	-0.63099	-0.63103
	(3.8554)	(3.6395)	(0.0287)	(0.9993)	(-0.49766)	(-0.63099)	
8.0	4.1012	3.8874	0.0267	0.9985	-0.49857	-0.62357	-0.62361
	(4.1046)	(3.8921)	(0.0265)	(0.9995)	(-0.49857)	(-0.62357)	
8.5	4.3481	4.1384	0.0246	0.9984	-0.49915	-0.61680	-0.61683
	(4.3528)	(4.1450)	(0.0244)	(0.9997)	(-0.49915)	(-0.61680)	
9.0	4.5948	4.3904	0.0227	0.9983	-0.49951	-0.61063	-0.61066
	(4.6005)	(4.3981)	(0.0224)	(0.9998)	(-0.49951)	(-0.61062)	

TABLE 4 (cont'd)

$R(a_0)$	$a$	$b$	$\alpha$	$\beta$	$E_p(e^2/a_0)$	$E_p - \frac{1}{R}(e^2/a_0)$	$(E - \frac{1}{R})(e^2/a_0)$ Exact
9.5	4.8413 (4.8477)	4.6434 (4.6513)	0.0208 (0.0206)	0.9983 (0.9999)	-0.49974 (-0.49974)	-0.60500 (-0.60500)	
10.0	5.0883 (5.0947)	4.8964 (4.9046)	0.0191 (0.0190)	0.9984 (0.9999)	-0.4988 (-0.49988)	-0.59988 (-0.59988)	
11.0	(5.5884)	(5.4113)	(0.0161)	(0.9999)	(-0.50000)	(-0.59091)	
12.0	(6.0822)	(5.9176)	(0.0137)	(0.9999)	(-0.50004)	(-0.58337)	
13.0	(6.5765)	(6.4234)	(0.0117)	(0.9999)	(-0.50005)	(-0.57697)	
14.0	(7.0713)	(6.9286)	(0.0101)	(0.9999)	(-0.50004)	(-0.57147)	
15.0	7.5623 (7.5666)	7.4284 (7.4333)	0.0089 (0.0088)	0.9993 (1.0000)	-0.50003 (-0.50003)	-0.56670 (-0.56670)	
16.0	(8.0625)	(7.9374)	(0.0078)	(1.0000)	(-0.50002)	(-0.56252)	
17.0	(8.5589)	(8.4411)	(0.0069)	(1.0000)	(-0.50002)	(-0.55884)	
18.0	(9.0556)	(8.9443)	(0.0061)	(1.0000)	(-0.50001)	(-0.55557)	
19.0	(9.5526)	(9.4473)	(0.0055)	(1.0000)	(-0.50001)	(-0.55264)	
20.0	10.0470 (10.0500)	9.9470 (9.9499)	0.0050 (0.0050)	0.9997 (1.0000)	-0.50001 (-0.50001)	-0.55001 (-0.55001)	

## LIST OF FIGURES

**Figure 1 (Page 33).**

The  $1s\sigma$  ground state energy of  $H_2^+$  is plotted as a function of R. --- represents the energy corresponding to the Pauling function<sup>14</sup>  
 $\chi_s = e^{-r_A} + e^{-r_B}$ . - - - represents the energy corresponding to the function,  
 $\phi_s = e^{-r_A - r_B}$ . "Exact" refers to the Bates, Ledsham and Stewart<sup>8</sup> solution of the exact differential equation.

**Figure 2 (Page 34).**

The  $2p\sigma$  first excited state energy of  $H_2^+$  is plotted as a function of R. "One parameter" represents the results of the one parameter variation. "Two parameters" represents the results of the two parameter variation. "Exact" corresponds to the Bates, Ledsham and Stewart<sup>8</sup> solution of the exact differential equation.

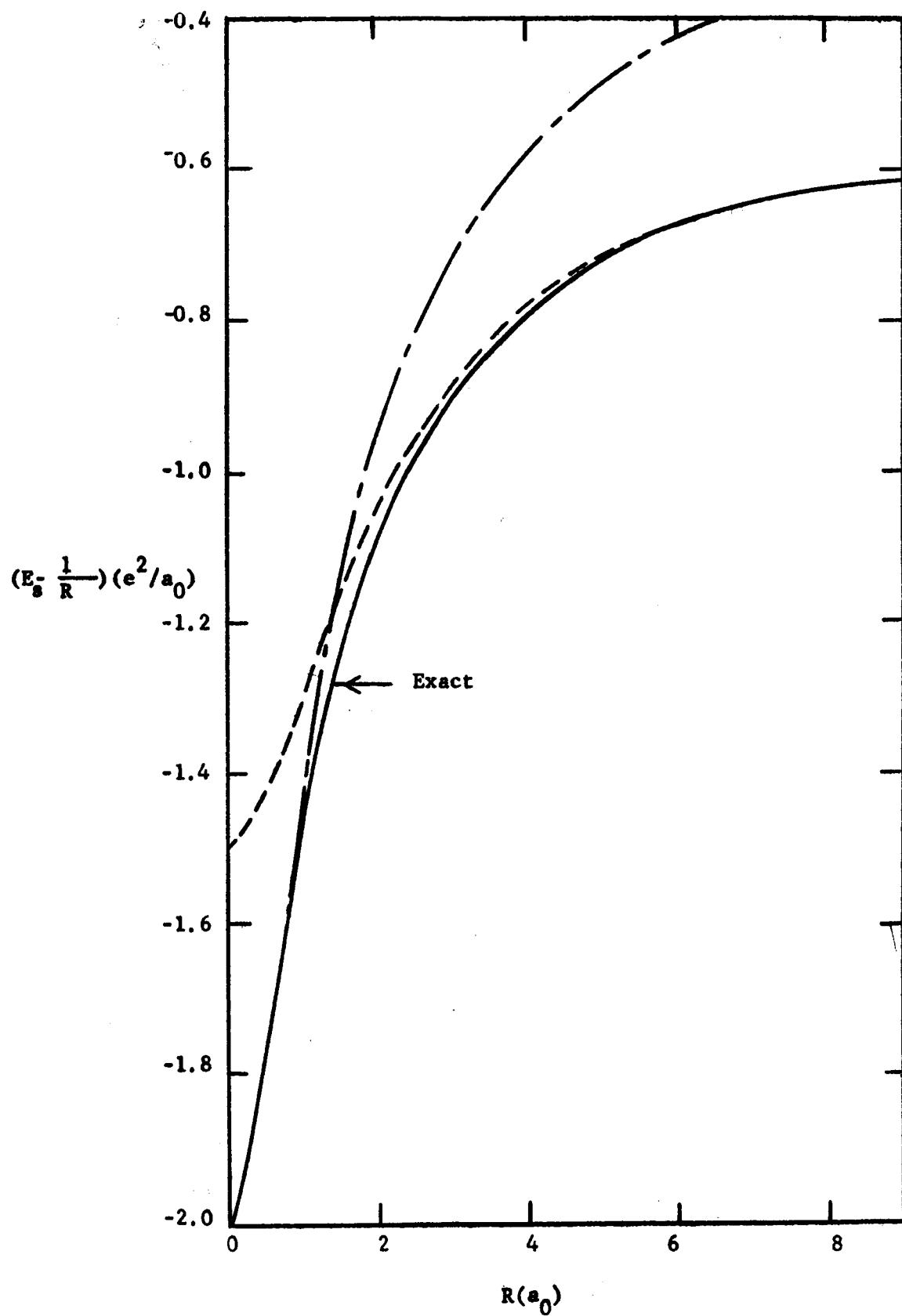


Fig. 1

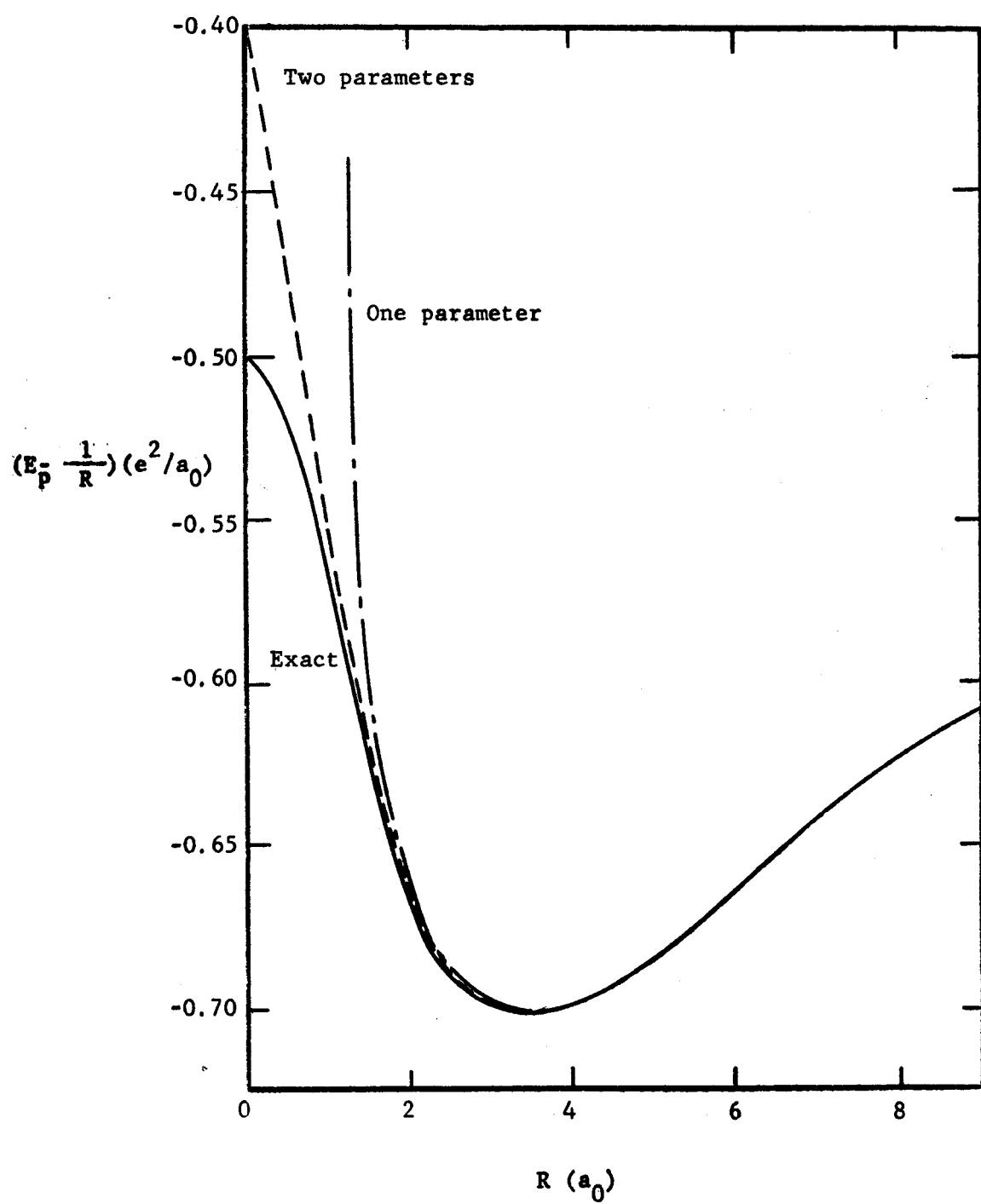


Fig. 2